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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁶ : C01B 3/48, 3/52</p>	<p>A1</p>	<p>(11) International Publication Number: WO 99/41188</p> <p>(43) International Publication Date: 19 August 1999 (19.08.99)</p>
<p>(21) International Application Number: PCT/EP98/00821</p> <p>(22) International Filing Date: 13 February 1998 (13.02.98)</p> <p>(71) Applicant (for all designated States except US): NORSK HYDRO ASA [NO/NO]; Bygdoy Alle 2, N-0240 Oslo (NO).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): SOYEZ, Werner [DE/BE]; Schuitenlaan 6, B-3080 Vossem (BE). SAIGNE, Michel [FR/BE]; Avenue Astrid 32, B-1640 Rhode-St.-Genèse (BE). KONGSHAUG, Gunnar [NO/NO]; Borgekroken 7, N-3711 Skien (NO).</p> <p>(74) Agent: BLEUKX, Luc; Hydro S.A., Marcel Thirylaan 83, B-1200 Brussel (BE).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report. With amended claims.</p>
<p>(54) Title: PROCESS FOR PRODUCING ELECTRICAL POWER AND STEAM</p> <p>(57) Abstract</p> <p>Process for producing electrical power and steam comprising steam reforming of a hydrocarbon feedstock and reduced CO₂ emission, where the gas mixture from the reforming reaction (50) is treated in a CO-shift (16, 20) and that the resulting gas is treated in a CO₂-absorption/separation unit for separation (30) into a concentrated CO₂-stream (32) and a gas stream comprising substantially hydrogen (33), part of which is combusted with air in a power generating turbine (44) and the remaining part is recycled for being used as fuel and that the exhaust from the turbine is recycled for combustion of at least part of this exhaust gas.</p>		

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Process for producing electrical power and steam.

The invention relates to a process for producing electrical power and steam comprising steam reforming of a hydrocarbon feedstock.

Such a process is generally known, see e.g. Japanese patent publication 6-80401.

- 5 According to this known process the hydrocarbon feedstock, such as natural gas, or light hydrocarbons is mixed with pure oxygen and supplied to a so-called autothermal reactor in which the mixture is reformed into hydrogen and carbon monoxide. The reformed gas enters a shift reactor in which the carbon monoxide is converted into carbon dioxide, and thereupon the gas mixture is introduced into a membrane separator in which the hydrogen is separated
10 from the carbon dioxide. The separated CO₂ is washed-out and desorbed later. The hydrogen substantially free from carbon compounds is used in a gas turbine for generating power.

- The object of this known process is to provide a power recovery type hydrogen generator having a high energy efficiency, which can self supply operating power for a PSA unit
15 producing oxygen from air for the combustion of the hydrocarbon feedstock, a hydrogen generator not releasing carbon dioxide, and a carbon dioxide free co-generating system having a high energy efficiency. The process requires oxygen, demanding a power consuming PSA unit. According to the flow sheet the natural gas must be decompressed nearly to ambient pressure to permit addition of oxygen. Also the oxygen after PSA
20 separation must be compressed a second time. All these extra compressions reduce the efficiency of the process.

- It is an object of the invention to provide an improved process for generating power using steam reforming of a hydrocarbon feedstock, in which on one hand the generated CO₂-gas is separated as a highly concentrated CO₂-gas stream, and on the other hand enough power
25 is generated to compete with power generating processes using hydrocarbon feedstock, but resulting in substantive emission of carbon dioxide to the environment.

These and other advantages are obtained in that the gas mixture from the steam reforming reaction is treated in a CO-shift converting unit and the resulting gas is treated in a CO₂-adsorption/separation unit for separation into a concentrated CO₂-stream and a gas

stream comprising substantially hydrogen, part of which is combusted with air in a power generating turbine and the remaining part is recycled for being used as fuel, and in that the exhaust from the turbine is recycled for combustion of at least part of this exhaust gas.

5 In this way a process has been obtained whereby the CO₂-emission to the environment has been reduced to less than 15% by weight of the CO₂ produced by the process, while maintaining the overall efficiency up to a level of at least 45%, which is an highly competitive value for this type of processes. More-over the produced CO₂ is obtained in a sufficiently concentrated form for being applied for other purposes, such as the production of urea, the use as injection gas in enhanced oil production or any other application requiring a relatively
10 pure CO₂-stream.

Other characteristics and advantages of the invention will become clear from the following description of an embodiment of the process according to the invention, reference being made to the annexed drawing. In the sole drawing there is shown schematically a flow-diagram of the process according to the invention.

15 As shown in the drawing natural gas is supplied through a line 1. As commonly used the natural gas is supplied at a defined temperature and an elevated pressure. In a heat exchanger 2 the natural gas is heated by means of steam or any other available heating supplying source, while maintaining the original supply pressure. The natural gas is further conducted through line 3 and subsequently decompressed in a turbine 4, and the so
20 generated energy is used in a electric power generating station 5.

This natural gas is now transported through a line 6 to mixing unit 7 in which the natural gas is mixed with steam. Steam is supplied through line 8. The amount of steam and natural gas mixed in the mixing device 7 are e.g. in a defined relationship in order to obtain a good reforming reaction further on. The obtained mixture steam/natural gas is supplied through
25 line 9 to a heat exchanger 10 heated by any available heat source, where the mixture is heated of a suitable temperature for the subsequent reforming reaction. This mixture is now supplied through line 11 to the part 12 of a reforming furnace 50, in which the mixture is lead over a suitable catalyst whereby the natural gas is converted into so-called synthesis-gas containing a high amount of hydrogen, CO and CO₂.

The obtained gas mixture is led through line 13, could through a heat exchanger 14 and from there through a line 15 to a high temperature conversion unit 16 in which part of the CO is converted into CO₂. In the heat exchanger 14 the gas mixture obtained by the reforming process is cooled and the so obtained heat energy can be used in some other place in the process. The gas mixture leaving the first converting unit 16 is supplied through line 17 to a heat exchanger 18 where it is cooled and subsequently fed through line 19 to a second converting unit 20. In the second converting unit the remaining CO in the gas mixture is converted into CO₂.

In the embodiment shown two converting reactors 16 and 20 have been provided in series, but alternatively it is also possible to use one single autothermal converting unit, in which the complete converting reaction is performed in one step.

The mixture leaving the second converting reactor 20 through line 21 is fed to a number of heat exchangers 22, 24 and 26 connected to each other through line 23 and 25. The number of heat exchangers is as such not important, as this is dependent upon the use of the heat. Basically it is enough to have one heat exchanger in which the gas mixture is cooled to a temperature which is low enough to have substantially all the water separated from the gas. In the embodiment shown heat exchanger 24 is in fact a reboiler for the purpose of CO₂-removal, whereas heat exchanger 26 is acting as a cooler.

In view however the energy content of the gas mixture after leaving the second converting reactor 20 it is recommendable to have more than one heat exchanger in order to optimize the energy recovered in the heat exchanger 22, 24 and 26.

The gas mixture leaving the heat exchanger 26 is fed through a line 27 to a separation unit 28 in which substantially all of the water is removed from the gas mixture, the water being drained through line 51. The gas substantially dry gas leaving at the top of the separation unit 28 is fed through line 29 to the bottom of an absorption unit 30. At the top of the absorption unit 30 there is a supply of absorption liquid, such as e.g. MDEA fed through line 31. The saturated absorption liquid, loaded with CO₂, is discharged at the bottom through line 32. This liquid mixture can be further treated in a desorption unit thereby separating the CO₂ from the absorption liquid which can be re-used. The specified CO₂-stream can be used for other purposes, such as feedstock for chemical processes or as driving gas in oil wells, natural gas fields, etc.

The purified gas mixture, contained substantially pure hydrogen leaves the absorption unit through line 33 and is fed to a separation unit 34 in which the gas is free from any remnants of the absorption liquid, which is drained through line 35. The dry and purified gas stream is further led through line 36 and is divided out into two lines, one line 37 and a second line 38.

5 The gas mixture in line 37 is at 39 mixed with air originating from line 40, which is in fact the exhaust line of a compressor 41 to which air is supplied through line 42. The so obtained gas mixture composed substantially of hydrogen, and air is supplied through line 43 to a hydrogen burning turbine 44, the output power of which being used for driving the compressor 41 and for generating electric energy in a power station 45.

10 As a result of the surplus of air supplied to the gas mixture at 39, the exhaust gas of the turbine 44 still contains a substantial amount of oxygen. This exhaust gas is fed through line 46 to the upper part 47 of the reforming reactor 50, where it is mixed with other gases and used in a heat exchanging process in order to recover the heat still available in this exhaust gas

15 Part of the exhaust gas flowing through line 46 is divided out of line 46 at 48 and is mixed with the gas mixture originating from line 38. This gas mixture containing hydrogen and oxygen is fed to the lower portion 12 of the reforming reactor and is burned there in order to generate heat for the reforming process. The burning gases therefrom are mixed with the gas originating from 46 and used for heat recovery in the upper part 47 of the reforming reactor. The so recovered heat is used to produce steam. This steam is expanded in a turbine thereby producing power. Part of the steam is used as a so-called process-steam, such as e.g. used in line 8.

The cooled exhaust gas is leaving the reforming reactor 50 through line 49.

25 A second reformer can be placed between the primary reformer 47 and the CO-conversion unit (16/20). The advantage of this being reduced CH_4 -slip and thereby reduction in CO_2 emission from the hydrogen turbine and accordingly from the total process.

The reformer 47 can of course be run as an autothermal reactor within the concept of the invention, but with some obvious alterations. However, one problem therewith is that it requires a cheap oxygen supply.

A further possible modification of the basic process comprises recycle of the reclaimed CO_2 . For any kind of disposal, the reclaimed CO_2 is to be compressed. Taking a bleed stream of CO_2 from e.g. an interstage cooler and recycling it to the reformer (line 6 or line 9) increases the overall efficiency and saves operating costs. This might be especially interesting in case
5 the installation is used in combination with an alkanol plant, especially methanol, as in this way an increased CO-content is available in line 13.

Example

In order to further elucidate the invention an example was worked out from which the thermodynamic characteristics in the different places of the process will become clear and also the composition of the different streams. In table 1A and 1B there are shown these data, the numbers indicating the columns correspond to the different places shown in the Figure.

Table 1A

	1	9	11	13	17	21
Molar total MMol/h	3.58	17.85	17.85	24.45	24.45	24.45
Gas Nm³/h	80,173	400,164.3	400,164.3	548,094.8	548,094.8	548,094.8
Gas dry Nm³/h				333,265.3	364,795	374,611.3
Mass T/h	61.81	319.07	319.07	319.05	319.05	319.04
Composition in % molar						
H₂	0	0	0	74.32	76.54	77.15
CH₄	93.21	18.68	18.68	3	2.74	2.67
C₂H₆	3.53	0.71	0.71			
C₃H₈	0.66	0.13	0.13			
C₄H₁₀	0.4	0.08	0.08			
C₅H₁₂	0.18	0.04	0.04			
CO	0	0	0	12.83	3.08	0.38
CO₂	0.3	0.06	0.06	9.43	17.26	19.43
N₂	1.72	0.34	0.34	0.41	0.38	0.37
O₂	0	0	0			
AR	0	0	0	0	0	0
H₂O	0	79.97	79.97	64.46	50.25	46.31
Temperature °C	5	340	650	850	403.2	220.7
Pressure bar	60	21.6	21.4	19.8	19.3	18.8

Table 1B

	36	42	46	47	49
Molar total MMol/h	13.58	74.82	80.11	21.96	82.55
Gas Nm ³ /h	304,386.8	1,677,098	1,795,558	492,204.8	1,850,196
Gas dry Nm ³ /h	302,064.5				
Mass T/h	38.99	2.167.199	0	550.52	2.217.446
Composition in % molar					
H ₂	95.68				
CH ₄	3.31				
C ₂ H ₆					
C ₃ H ₈					
C ₄ H ₁₀					
C ₅ H ₁₂					
CO	0.47				
CO ₂	0.08	0.03	0.45	1.22	0.66
N ₂	0.46	78.09	72.99	64.98	70.86
O ₂		20.95	13.52	0.5	10.06
AR	0	0.93	0.87	0.77	0.84
H ₂ O	0.77	0	12.16	32.53	17.58
Temperature °C	55	1	584	950	50
Pressure bar	18	1	1	1	1

- From this example it becomes clear that the CO₂ - content in the exhaust gas has been reduced to 0,66 % by weight, which corresponds to a reduction by 80 - 90 % by weight compared with the amount CO₂ actually generated by comparable the processes. The amount CO₂ in the exhaust gas is thereby brought to a level which is almost close to the normal presence of CO₂ in ambient air. Moreover the electrical power generated by the process as shown in the example is equal to 400 MW corresponding to an overall efficiency of 46% .

Claims

1. Process for producing electrical power and steam comprising steam reforming of a hydrocarbon feedstock and reduced CO₂ emission, characterized in that the gas mixture from the reforming reaction is treated in a CO-shift and that the resulting gas is treated in a
5 CO₂-absorption/separation unit for separation into a concentrated CO₂-stream and a gas stream comprising substantially hydrogen, part of which is combusted with air in a power generating turbine and the remaining part is recycled for being used as fuel and that the exhaust from the turbine is recycled for combustion of at least part of this exhaust gas.
2. Process according to claim 1, characterized in that at least part of the exhaust gas from the
10 power generating turbine is recycled to the reformer for serving as oxygen source.
3. Process according to claim 1, characterized in that the off-gas from the reformer is applied in a waste heat boiler together with the exhaust gas from the power generating turbine.
4. Process according to claim 1, characterized in that a second reformer is integrated in the
15 process between the primary reformer and the CO-shift unit for reducing the CH₄-slip from the reformer.
5. Process according to claim 1, characterized in that part of the gas stream comprising mainly hydrogen is recycled to the reformer as fuel source.
6. Process according to claim 1, characterized in that the generated hydrogen and carbon monoxide are used in combination with a chemical process making use of H₂ and /or CO.
- 20 7. Process according to claim 1, characterized in that during the reforming reaction a steam to carbon ration of 3,4 - 4,0 is applied.
8. Process according to claim 1, characterized in that the CO-shift reaction is performed in a single iso-thermal shift reactor.
9. Process according to claim 1, characterized in that all steam generated in the process, except
25 that used in the steam reforming unit, is used in a main stream turbine.

10. Process according to claim 1, characterized in that at least part of the reclaimed CO_2 is recycled to the reformer.

AMENDED CLAIMS

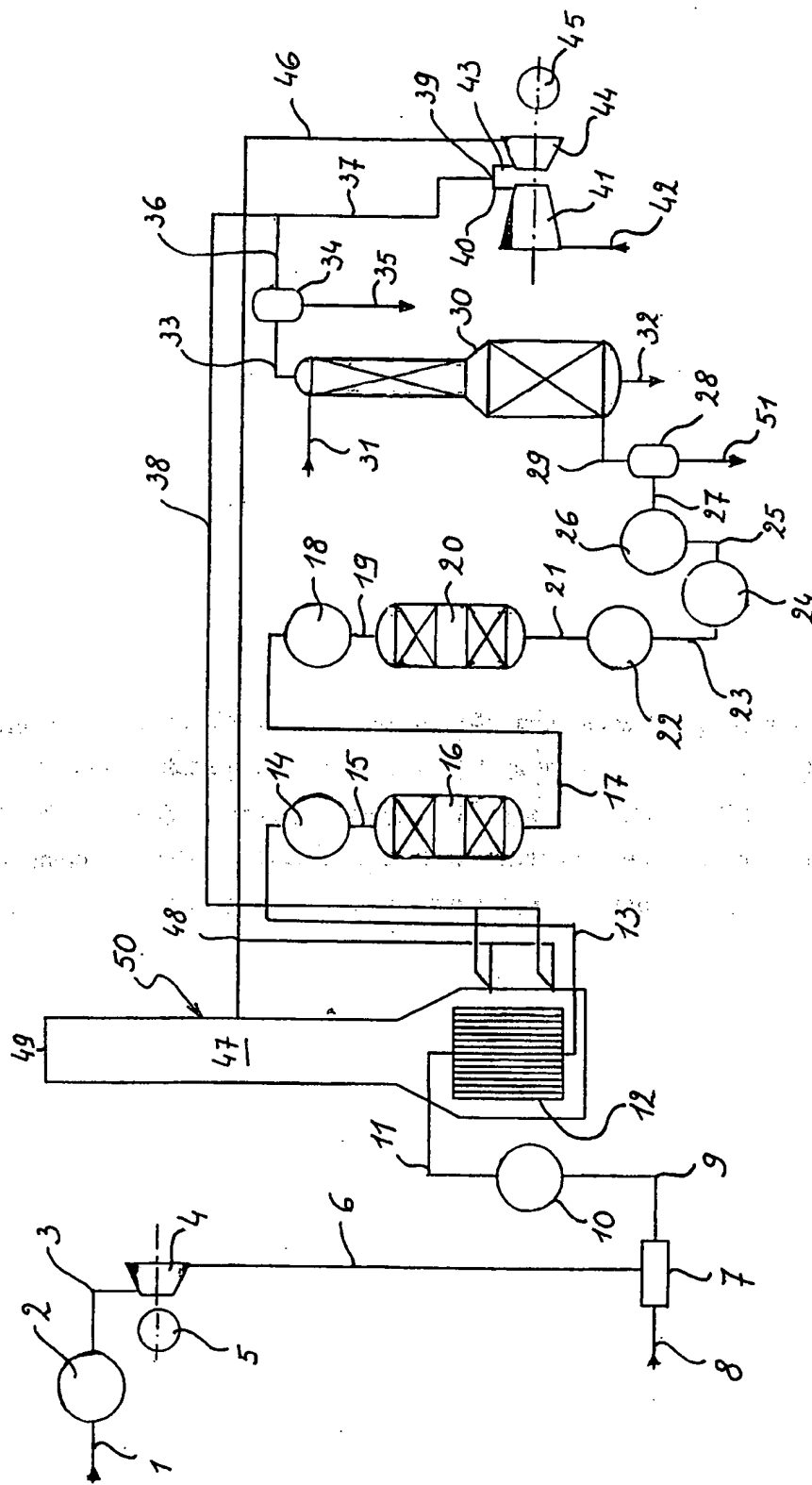
[received by the International Bureau on 12 March 1999 (12.03.99);
original claims 1, 4, 5, 7 and 9 amended; remaining claims unchanged (2 pages)]

1. Process for producing electrical power and steam comprising steam reforming of a hydrocarbon feedstock wherein the gas mixture from the reforming reaction is treated in a CO-shift and the resulting gas is treated in a CO₂-absorption / separation unit for separation into a concentrated CO₂-stream and a gas stream comprising substantially hydrogen, characterized in that part of the hydrogen is combusted with air in a power generating turbine and the remaining part is recycled for being used as fuel in the steam reforming process step and that part of the exhaust gas from the turbine is recycled to the steam reforming for further combustion thereof.
- 10 2. Process according to claim 1, characterized in that at least part of the exhaust gas from the power generating turbine is recycled to the reformer for serving as oxygen source.
- 15 3. Process according to claim 1, characterized in that the off-gas from the reformer is applied in a waste heat boiler together with the exhaust gas from the power generating turbine.
4. Process according to claim 1, characterized in that a second reformer is integrated in the process between the primary reformer and the CO-shift unit.
5. Process according to claim 1, characterized in that part of the gas stream comprising mainly hydrogen is recycled to the reformer.
- 20 6. Process according to claim 1, characterized in that the generated hydrogen and carbon monoxide are used in combination with a chemical process making use of H₂ and /or CO.
7. Process according to claim 1, characterized in that during the reforming reaction a steam to carbon ratio of 3,4 - 4,0 is applied.
8. Process according to claim 1, characterized in that the CO-shift reaction is performed in a single iso-thermal shift reactor.
- 25

AMENDED SHEET (ARTICLE 19)

9. Process according to claim 1, characterized in that all steam generated in the process, except that used in the steam reforming unit, is used in a main steam turbine.

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INTERNATIONAL SEARCH REPORT

Intern al Application No

PCT/EP 98/00821

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01B3/48 C01B3/52

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 413 199 A (SIEMENS AG) 20 February 1991 see column 1, line 30 - column 3, line 1 see claim 1	1
X	US 4 690 812 A (RANKE GERHARD ET AL) 1 September 1987 see the whole document	1,4
X	US 3 656 905 A (SMITH CALVIN S ET AL) 18 April 1972 see column 7, line 38 - column 8, line 40 see figure	1
X	US 3 382 045 A (HABERMEHL ROBERT H ET AL) 7 May 1968 see column 3, line 58 - column 4, line 20 see figures	1,4

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

6 October 1998

Date of mailing of the international search report

16/10/1998

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>PATENT ABSTRACTS OF JAPAN vol. 018, no. 337 (C-1217), 27 June 1994 & JP 06 080401 A (MITSUI ENG & SHIPBUILD CO LTD), 22 March 1994 cited in the application see abstract</p> <p>-----</p>	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat

Application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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